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**(54) Method for the production of thermoplastic polyurethanes**

(57) A method for the production of thermoplastic polyurethanes with a Vicat temperature of  $\geq 140$  °C, a Shore hardness of 70 A to 55 D and a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$ , by reaction of (a) isocyanates with (b) compounds that are reactive to isocyanates and have a molecular weight of 500 to 8000 in the presence of (c) chain lengthening agents with a molecular weight of 60 to 499 and optionally (d) catalysts and/or (e) common auxiliary agents and/or additives, wherein aliphatic and/or cycloaliphatic isocyanates are used as the isocyanates (a), and at least one araliphatic, aromatic and/or cycloaliphatic compound is used as the chain lengthening agent (c).

## Description

[0001] The invention concerns a method for the production of thermoplastic polyurethanes with a Vicat temperature of  $\geq 140$  °C, preferably  $\geq 150$  °C, most preferably 160 to 250 °C, a Shore hardness of 70 A to 55 D and a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$ , preferably  $< 10$ , most preferably 4 to 9.9, by reaction of (a) isocyanates with (b) compounds that are reactive to isocyanates and have a molecular weight of 500 to 8000 in the presence of (c) chain lengthening agents with a molecular weight of 60 to 499 and optionally (d) catalysts and/or (e) common auxiliary agents and/or additives as well as the thermoplastic polyurethanes that can be produced with this method and their use.

[0002] Thermoplastic polyurethanes, also denoted TPUs in the following, as well as methods for their production are known in general and have been described many times. These TPUs are partially crystalline materials and belong to the class of thermoplastic elastomers. They are comprised of a partially crystalline hard block, which is constructed of the isocyanate and low-molecular chain lengtheners, and an amorphous soft block, which is typically constructed of high-molecular compounds reactive to isocyanates, usually polyesters and/or polyether diols. A micromorphological segregation of these phases that is as complete as possible is the necessary prerequisite for the elastic behavior of the TPUs. Due to its partial crystallinity, the hard block acts as a physical crosslinking, which is reversible above the hard-block melting point, and this makes possible the thermoplastic deformation of the material. The soft

block is found at room temperature in a plastic or liquid state, and the easy deformability of the TPU can finally be attributed to this. The physical crosslinking thus makes possible the elastic return to the initial state.

[0003] TPUs are characterized by a combination of advantageous material properties, such as, for example, little wear due to abrasion, a good resistance to chemicals as well as a high flexibility with a simultaneously high strength. TPUs based on aliphatic raw materials additionally have the advantage of a particularly good resistance to light. In addition, they offer advantages due to cost-favorable production, for example, with the strip or the extruder process, which can be conducted continuously or discontinuously, and simple thermoplastic processing.

[0004] Due to variation of the initial components, products with a broad palette of properties can be produced in a wide hardness region. The heat shape stability and thus also the use properties of the material at temperatures particularly above 80 °C and thus the quality of the physical crosslinking are predominantly determined by the melting behavior of the hard segment block. The resistance to light of the materials depends on the content of aromatic structural units.

[0005] Thermoplastic polyurethanes, which are usually produced on the basis of (a) MDI, (b) polyester and/or polyether diols and (c) butanediol, typically partially lose their heat shape stability above 80 °C, i.e., the material no longer reversibly returns to its initial state. In order to be able to use TPUs under static or dynamic loads at higher

application temperatures, the heat shape stability must be improved in comparison to known TPUs. In addition, TPUs which are based on MDI as the isocyanate, have the disadvantage that they turn yellow in daylight after longer use. This effect is undesired in applications subject to such exposure. This problem can be avoided by the use of aliphatic isocyanates. TPUs based on aliphatic isocyanates, however, in comparison to those based on aromatic isocyanates, have the disadvantage that they have a clearly lower heat shape stability. The heat shape stability and thus also the use properties of the material are determined predominantly by the melting behavior of the hard segment block at higher temperatures. For the hard phases of TPUs based on aliphatic isocyanates, the melting points of these hard phases are clearly lower than the hard phases of TPUs which are based on aromatic isocyanates. A material would be desirable, which simultaneously has the resistance to light of TPUs based on aliphatic isocyanates and the heat shape stability of TPUs based on aromatic isocyanates.

[0006] An improvement of the heat shape stability of TPUs brought about by the use of aromatic chain lengthening agents is described in EP-A 718,335. The deficient resistance to light of the TPUs described in the Examples of this document acts as a disadvantage. GB 1,126,963 describes TPUs based on substituted hexamethylene diisocyanate as well as aliphatic, cycloaliphatic or aromatic chain lengthening agents (claim 6 in combination with claim 1). A technical teaching for improvement of the heat shape stability or the resistance to light of a TPU is not given in GB 1,126,963.

[0007] The object of the present invention was thus to develop a method for the production of thermoplastic polyurethanes by reaction of (a) isocyanates with (b) compounds that are reactive to isocyanates and have a molecular weight of 500 to 8000 in the presence of (c) chain lengthening agents with a molecular weight of 60 to 499 and optionally (d) catalysts and/or (e) common auxiliary agents and/or additives, with which light-resistant products with a very good heat shape stability can be obtained, i.e., thermoplastic polyurethanes with a Vicat temperature of  $\geq 140$  °C, a Shore hardness of 70 A to 55 D and a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$ .

[0008] This object could be solved in that aliphatic and/or cycloaliphatic, preferably aliphatic isocyanates are used as the isocyanates (a), and at least one araliphatic, aromatic and/or cycloaliphatic, preferably araliphatic and/or aromatic compound is used as the chain lengthening agent (c).

[0009] Methods for the production of TPUs are generally known and are distinguished from methods for the production of polyisocyanate polyaddition products which cannot be processed thermoplastically principally by the fact that one extensively avoids chemical crosslinkings in the product and thus uses as compounds (b) reactive to isocyanates, preferably those which have a mean functionality of 1.8 to 2.6, most preferably 1.9 to 2.2, particularly 2, and preferably extensively dispenses with crosslinking agents, i.e., compounds reactive to isocyanates with a molecular weight of  $< 499$  and a functionality of  $\geq 3$ , and most preferably dispenses with these completely.

[0010] In the following, as an example, the initial components and methods for the production of preferred TPUs will be presented.

[0011] The components (a), (b), (c) usually used in the production of TPUs as well as optionally (e) and/or (f) will be described below by way of example:

a) Aliphatic and/or cycloaliphatic isocyanates are utilized as organic isocyanates (a), for example, tri-, tetra-, penta-, hexa-, hepta- and/or octamethylene diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2-ethylbutylene 1,4-diisocyanate, pentamethylene 1,5-diisocyanate, butylene 1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), 1,4- and/or 1,3-bis(isocyanatomethyl)cyclohexane (HXDI), 1,4-cyclohexane diisocyanate, 1-methyl-2,4- and/or 2,6-cyclohexane diisocyanate and/or 4,4'-, 2,4'- and 2,2'-dicyclohexylmethane diisocyanate. Preferably, hexamethylene 1,6-diisocyanate (hexamethylene diisocyanate, HDI) is utilized as the isocyanate.

b) For example, polyhydroxy compounds with molecular weights of 500 to 8000, preferably 600 to 6000, in particular 800 to 4000, and preferably with a mean functionality of 1.8 to 2.6, preferably 1.9 to 2.2, particularly 2, can be utilized as compounds (b) reactive to isocyanates. Preferably, one uses as (b) polyesterols and/or polyetherols (and/or polycarbonate diols). most preferably polyester diols, for example, polycaprolactone, and/or polyether polyols, for example those based on ethylene oxide,

propylene oxide and/or butylene oxide, preferably polypropylene glycol, in particular, polyetherols.

c) Araliphatic, aromatic and/or cycloaliphatic, preferably araliphatic and/or aromatic compounds with a molecular weight of 60 to 499, are utilized as chain lengthening agents (c) according to the invention, preferably 2-function compounds, preferably substituted benzenes, most preferably 1,4-, 1,3- and/or 1,2-bis(3-hydroxypropyl)benzene, 1,4-, 1,3- and/or 1,2-bis(2-hydroxyethyl)benzene, 1,4-, 1,3- and/or 1,2-bis(2-hydroxyethoxy)benzene and/or 1,2-, 1,3- and/or 1,4-bis(hydroxymethyl)benzene, most preferably 1,3- and/or 1,4-bis(hydroxymethyl)benzene.

Optionally, other generally known chain lengtheners (ci) can be utilized in addition to the chain lengthening agents (c) according to the invention, for example, diamines and/or alkanediols with 2 to 10 C atoms in the alkylene group, in particular 1,4-butanediol and/or di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and/or deca-alkylene glycols with 3 to 8 carbon atoms, preferably corresponding oligo- and/or polypropylene glycols, wherein mixtures of chain lengtheners can also be utilized. Most preferably, the chain lengthening agents according to the invention are utilized exclusively.

d) Suitable catalysts, which in particular accelerate the reaction between the NCO groups of the diisocyanates (a) and the hydroxyl groups of the structural components (b) and (c) are the usual tertiary amines and are known in the prior art, such as e.g.,

triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminoethoxy)ethanol, diazabicyclo [2.2.2] octane and similar compounds as well as, in particular, organometallic compounds such as titanate acid esters, iron compounds such as, e.g., iron(III) acetylacetonate, tin compounds such as, e.g., tin diacetate, tin dioctoate, tin dilaurate or tin dialkyl salts of aliphatic carboxylic acids such as dibutyltin diacetate, dibutyltin dilaurate or similar compounds. The catalysts are usually utilized in quantities of 0.0001 to 0.1 weight parts per 100 weight parts of polyhydroxy compound (b).

e) In addition to catalysts, the usual auxiliary agents and/or additives (e) can also be added to the structural components (a) to (d). The following will be named by way of example: surfactants, fillers, flameproofing agents, nucleation agents, oxidation stabilizers, stabilizers, slip and demolding aids, dyes and pigments, inhibitors, stabilizers against hydrolysis, light, heat, or discoloration, agents protecting against microbial attack, inorganic and/or organic fillers, reinforcing agents and plasticizers.

[0012] Detailed information on the above-named auxiliary agents and additives can be taken from the professional literature.

All molecular weights named in this publication are in [g/mol] units.

[0013] In order to adjust the hardness of the TPUs, the structural components (b) and (c) can be varied in relatively broad molar ratios. Molar ratios of component (b) to the total



amount of chain lengthening agents (c) utilized of 1: 0.5 to 1:8, in particular of 1:1 to 1:4, wherein the hardness of the TPU increases with increasing content of (c), have proven suitable.

[0014] The reaction can be produced with the usual characteristic numbers, preferably with a characteristic number from 90 to 120, most preferably with a characteristic number from 97 to 115. The characteristic number is defined by the ratio of the total number of isocyanate groups of component (a) utilized in the reaction to the groups [reactive] to the isocyanates, i.e., the active hydrogens, of components (b) and (c). A characteristic number of 100 indicates that one active hydrogen atom, i.e., one function reactive to isocyanates, of components (b) and (c) arrives at one isocyanate group of component (a).

[0015] With characteristic numbers greater than 100, there are more isocyanate groups present than OH groups.

[0016] The isocyanate index, also named characteristic number, is the number of isocyanate groups actually used divided by the number of isocyanate groups theoretically necessary for the complete reaction of all OH groups multiplied by 100.

[0017] TPUs can be produced according to known processes continuously with reaction extruders or discontinuously according to the known prepolymer process. In these

processes, the components (a), (b) and optionally (c) entering into the reaction can be mixed together successively or simultaneously, whereby the reaction proceeds directly.

[0018] Preferably, the reaction is conducted in the reaction extruder.

[0019] As has already been presented, the reaction mixture containing (a), (b), (c) und optionally (d) and/or (e) can be reacted preferably according to the extruder process or according to the prepolymer process or in the laboratory, also according to the one-shot process.

[0020] In the extruder process, the structural components (a) to (c) as well as optionally (d) and/or (e) are introduced into the extruder individually or as a mixture, e.g., at temperatures of 100 to 250 °C, preferably 140 to 220 °C, brought to reaction, and the TPU obtained is extruded, cooled and granulated.

[0021] The processing of the TPUs produced according to the invention, which are usually present as granulate or in powder form, is conducted according to the usual methods such as, e.g., injection molding or extrusion, to produce the desired foils, fibers, molded parts, moldings in automobiles, rolls, gaskets, cable connectors, shock absorbers, flexible tubings, cable sheathing, trailing cables, belts or damping elements, particularly foils.

[0022] The thermoplastic polyurethanes that can be produced according to the methods according to the invention, particularly foils, fibers, molded parts, moldings in automobiles, rolls, gaskets, cable connectors, shock absorbers, flexible tubings, cable sheathing, trailing cables, belts or damping elements, particularly foils, have the desired high heat shape stability, characterized by a Vicat temperature of  $\geq 140$  °C, preferably  $\geq 150$  °C, a Shore hardness of 70 A to 55 D and a high resistance to light, characterized by a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$ , preferably  $< 10$ .

[0023] Both the high heat shape stability for a TPU based on (cyclo)aliphatic isocyanates as well as also the very good resistance to light in comparison to TPUs based on aromatic isocyanates were surprising to the person skilled in the art. For the preferred use of aromatic chain lengthening agents, it was obvious to assume that the TPUs would have a tendency toward yellowing, which would be comparable to that of TPUs based on aromatic isocyanates. The very high resistance to light according to the invention was not expected.

[0024] The advantages according to the invention will be presented on the basis of the following examples.

## Production of TPUs

### Example 1

[0025] A mixture containing 179.8 g of Lupranol® VP 9066 (BASF Aktiengesellschaft) and 20 ppm of dibutyltin dilaurate (Merck-Schuchla), which was heated to 110 °C, was brought to reaction while stirring with 32.03 g of hexamethylene diisocyanate. After reaction, 8.17 g of 1,4-butanediol were added at an increased stirring speed for a time of 30 min at the same temperature. After reaching a temperature in the reaction mixture of 120 °C, the mixture was poured into a flat dish and hardened for 20 min at 120 °C. After tempering for 24 h at 100 °C, the material was granulated and processed into test samples by means of injection molding.

#### Example 2

[0026] A mixture containing 164.97 g of Lupranol® VP 9066 (BASF Aktiengesellschaft) and 16.07 g of 1,4-butanediol, which was heated to 100 °C, was brought to reaction while stirring with 68.97 g of MDI, which was added to the mixture at a temperature of 50 °C. After reaching a temperature in the reaction mixture of 120 °C, the mixture was poured into a flat dish and hardened for 20 min at 120 °C. After tempering for 24 h at 100 °C, the material was granulated and processed into test samples by means of injection molding.

#### Example 3

[0025] A mixture containing 162.07 g of Capa® 223 (Solvay Interlox), 29.86 g of 1,4-bis(hydroxymethyl)benzene and 20 ppm of dibutyltin dilaurate (Merck-Schuchla), which

was heated to 110 °C, was brought to reaction while stirring with 53.07 g of hexamethylene diisocyanate. After reaching a temperature in the reaction mixture of 120 °C, the mixture was poured into a flat dish and hardened for 20 min at 120 °C. After tempering for 24 h at 100 °C, the material was granulated and processed into test samples by means of injection molding.

[0028] The properties of the TPUs are shown in Table 1.

Table 1

Example:	1	2	3
Hardness Shore A	87	85	90
Vicat temperature [°C]	50	136	168
Yellowness Index according to DIN 54004 (after 45 h)	10.4	23.7	9.8
Yellowness Index according to DIN 54004 (after 168 h)	10.3	61.5	9.4
Yellowness Index according to DIN 54004 (after 228 h)	10.5	76.4	8.6
Yellowness Index according to DIN 54004 (after 504 h)	11.4	90.1	9.0

[0029] TPUs based on hexamethylene diisocyanate (Example 1) usually have a clearly lower heat shape stability in comparison to TPUs based on MDI (Example 2).

Surprisingly, the TPUs according to the invention according to Example 3 in fact show a better heat shape stability than TPUs based on MDI. The improved heat shape stability could also be detected on the basis of torsional vibration curves. Additionally, the targeted object of developing TPUs with resistance to light could be achieved. The TPU of Example 3 according to the invention shows clearly less yellowing than the comparative product of Example 1. As another advantage of the material according to the invention, it can be stated that, in contrast to the TPU of Example 1, no

efflorescence of low-molecular reaction products, i.e., migration from the TPU, could be observed.

## Patent Claims

1. A method for the production of thermoplastic polyurethanes with a Vicat temperature of  $\geq 140$  °C, a Shore hardness of 70 A to 55 D and a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$  by reaction of (a) isocyanates with (b) compounds that are reactive to isocyanates and have a molecular weight of 500 to 8000 in the presence of (c) chain lengthening agents with a molecular weight of 60 to 499 and optionally (d) catalysts and/or (e) common auxiliary agents and/or additives, is hereby characterized in that aliphatic and/or cycloaliphatic isocyanates are used as the isocyanates (a), and at least one araliphatic, aromatic and/or cycloaliphatic compound is used as the chain lengthening agent (c).
2. The method according to claim 1, further characterized in that aliphatic isocyanates are used as (a).
3. The method according to claim 1, further characterized in that substituted benzenes are used as (c).
4. The method according to claim 1, further characterized in that one uses as (c) 1,4-, 1,3- and/or 1,2-bis(3-hydroxypropyl)benzene, 1,4-, 1,3- and/or 1,2-bis(2-hydroxyethyl)benzene, 1,4-, 1,3- and/or 1,2-bis(2-hydroxyethoxy)benzene and/or 1,2-, 1,3- and/or 1,4-bis(hydroxymethyl)benzene.

5. The method according to claim 1, further characterized in that 1,3- and/or 1,4-bis(hydroxymethyl)benzene is used as (c) .
6. The method according to claim 1, further characterized in that the reaction is conducted with a characteristic number of 97 to 115.
7. Thermoplastic polyurethanes with a Vicat temperature of  $\geq 140$  °C, a Shore hardness of 70 A to 55 D and a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$  obtainable by a method according to one of claims 1 or 6.
8. Use of hexamethylene diisocyanate and 1,3- and/or 1,4-bis(hydroxymethyl)benzene for the production of thermoplastic polyurethanes with a Vicat temperature of  $\geq 140$  °C, a Shore hardness of 70 A to 55 D and a Yellowness Index according to DIN 54004 after 504 hours of  $\leq 10$ .
9. Use of thermoplastic polyurethanes according to claim 7 as foils, molded parts, rolls, fibers, moldings in automobiles, flexible tubings, cable connectors, shock absorbers, trailing cables, cable sheathing, gaskets, belts or damping elements.
10. Foils, molded parts, rolls, fibers, moldings in automobiles, flexible tubings, cable connectors, shock absorbers, trailing cables, cable sheathing, gaskets, belts or damping elements containing thermoplastic polyurethanes according to claim 7.



# EP 1,028,132 A1

European Patent Office

EUROPEAN SEARCH REPORT

Number of the Application

EP 00 10 0899

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Category	Citation of the document, with indication, if necessary of the pertinent parts	Claim concerned	Classification of the application examined (Int. Cl.7)
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A	US 4,010,146 A (RUSSELL DAVID D ET AL) March 1, 1977 (1977-03-01) *Sentence 35 – Column 2, line 65* *claims 1, 7; Example 1*	1, 3, 4, 7, 9, 10	
A	EP 0 138,277 (GOODRICH CO BF) April 24, 1985 (1985-04-24) *page 1, line 14 – line 21* *page 11 – page 13; Example II	1, 2, 7, 9, 10	
D, A	EP 0,718,335 A (BAYER AG) June 26, 1996 (1996-06-26) *Claims 1-3*	1, 3, 4	

Technical fields  
searched (Int. Cl.7)  
C08G

The present search report was prepared for all patent claims.

Place of Search	Date of search completion	Searcher
The Hague	May 10, 2000	Neugebauer, U

## CATEGORY OF THE DOCUMENTS CITED

X: particularly pertinent alone

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A: pertinent against at least one claim or general technical background

O: nonwritten disclosure

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T: theory or principle upon which the invention is based

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L: cited for other reasons

&: member of the same patent family, corresponding document.

**ATTACHMENT TO THE EUROPEAN SEARCH REPORT  
RELATIVE TO THE EUROPEAN PATENT APPLICATION NO. EP 00 10 0899**

The present attachment indicates the members of the patent family relating to the patent documents cited in the European Search Report given above.

The data of said members are contained in the information file of the European Patent Office on the date of ... May 10, 2000

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For more details relative to this Attachment:

See: Office Bulletin of the European Patent Office, No. 12/82.